Factors affecting degradation rates of five triazole fungicides in two soil types: 2. Field studies

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Abstract: The criteria for registering pesticides persistent in soil are still a matter of debate. Amongst modern pesticides, several triazole fungicides are very persistent, though no deleterious effects on soil microbial processes have been reported. The behaviour of five such compounds (flutriafol, epoxiconazole, propiconazole, triadimefon and triadimenol) has been examined in two field trials utilising different agronomic treatments. These fungicides were applied in June 1996 at rates of 0.5 kg ha^{-1}, and soil cores were taken to 20 cm depth at intervals over 2.5 years and analysed by extraction and high-pressure liquid chromatography. Triadimefon was quite rapidly reduced to triadimenol. Triadimenol, flutriafol and epoxiconazole were all very persistent with $DT_{50} > 400$ days, whilst propiconazole had DT_{50} *c* 200 days; behaviour was similar in the Rothamsted clay loam and Woburn sandy loam. Only flutriafol, the most polar and hence weakly sorbed of these fungicides, was appreciably leached, with traces reaching the 15–20 cm deep soil layer. Sprays applied to plots of fallow soil suffered loss of up to 50% of applied compound in the first four weeks, a loss eliminated by shallow incorporation, indicating an early role for surface loss processes such as photolysis and/or volatilisation. A young barley crop intercepted about one-third of the spray, though subsequent rain caused some wash-off. After one to two years, amounts of each compound remaining in the plots were similar for the three agronomic treatments, especially for flutriafol, though with a tendency for the incorporated plots to have the most chemical and the barley plots the least. Computer simulation of behaviour in the field using the model CALF, utilising sorption and degradation measurements made in laboratory incubations with these same soils together with daily climate measurements, overestimated persistence especially for flutriafol, epoxiconazole and triadimenol. This was due both to lack of inclusion of surface loss processes in the model, which caused initial deviations in the plots not receiving cultivation after spraying, and to a longer-term underestimation of breakdown in the field. This latter was especially noticeable for triadimenol, which was not detected after 2.5 years despite predictions of *c* 50% remaining. Thus field measurements of behaviour are desirable, as simulations based on laboratory measurements can overestimate persistence.

Keywords: flutriafol; epoxiconazole; propiconazole; triadimefon; triadimenol; triazole fungicides; persistence in soil

1 INTRODUCTION

The long persistence in soil of the widely used triazole class of fungicides is a possible cause of concern in registering these compounds. In a companion paper, Bromilow *et al*[1] review such behaviour and report on the factors influencing the breakdown in soil in laboratory tests of five triazole fungicides.

Persistence in the field could lead to accumulation following repeated applications, to leaching to aquifers and drains or to deleterious effects on soil microbial processes. However, these compounds are at least moderately lipophilic and so moderately to strongly sorbed to soil, as assessed by Jamet and Eudeline[2] using soil thin-layer chromatography of 17 triazole fungicides. Flutriafol is the most polar of the commercial triazole fungicides, and Wechsler *et al*[3] observed it to be moderately mobile in soil. These compounds have not generally been found in water supplies, though triadimefon, when applied at very high rates to soil mesocosms under irrigation, did give rise to up to 616 μg litre^{-1} of triadimenol in leachate.[4] Furthermore, triadimenol was reported not to be accumulated in field soils[5] following 12 years application of triadimefon, nor have these repeated applica-

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tions of triadimefon[5] or high rates of epoxiconazole[6] influenced overall microbial activity in soil.

This paper studies the behaviour of five triazole fungicides (flutriafol, epoxiconazole, propiconazole and triadimefon, together with triadimenol derived from transformation in soil of the latter) at two field sites in plots receiving different cultivations and cropping. Using the complementary laboratory measurements on sorption and persistence,[1] comparisons are made between the predicted and observed behaviours of these compounds in the field in order to indicate any additional factors influencing their field behaviour. Coincidentally, Montfort *et al*[7] started in 1995 a three-year field study with five sterol-biosynthesis-inhibiting fungicides, including epoxiconazole and propiconazole common to our trials, and preliminary results indicated slow breakdown of the triazole fungicides.

2 MATERIALS AND METHODS

2.1 Field plots

Trials were on a clay loam soil on Foster's Corner, Rothamsted and on a sandy loam soil on Road Piece, Woburn, Bedfordshire. Details of the soils have been given previously.[1] Each trial was a randomised design of six plots, comprising duplicate plots (15.0×4.5 m) of three agronomic treatments. One pair of plots grew spring barley (*Hordeum vulgare* L cv Cooper) and the other four fallow plots were lightly cultivated prior to fungicide application. The barley crop was cultivated according to good agricultural practice but excluding fungicides, and after the first season these plots were left in stubble. These and the fallow plots received only occasional glyphosate treatment to keep them free of weeds.

2.2 Fungicide application to the plots

All plots received the four triazole compounds. Each fungicide was applied separately at 0.5 kg AI ha^{-1} using two passes of a tractor-mounted hydraulic sprayer and commercial formulations (Pointer, Opus, Bayleton and Tilt) of the compounds (flutriafol, epoxiconazole, triadimefon and propiconazole, respectively). This rate of application is equivalent to the likely maximum cumulative amount applied annually for each compound. Before application, filter-paper discs (80 mm diam, five per plot) were placed on the ground equidistantly spaced along a plot diagonal to collect the spray and so to check the application rates. After application on 4 June 1996 at Rothamsted and on 7 June 1996 at Woburn, on one pair of fallow plots the fungicides were shallowly incorporated by a single pass of a Roterra set to *c*7 cm depth. The spring barley was at Zadoks growth stage 25 at Rothamsted and 37 at Woburn.

2.3 Weather

Rainfall, evaporation from an open pan and air and soil temperatures (at 10 cm depth) were recorded daily at the two sites.

2.4 Soil sampling

Soil cores were taken using ABS-plastic sampling tubes, of wall thickness 5 mm and ID 76 mm. These were assembled by taping together rings of length 5.0 cm to give tubes of length, 10, 15 or 20 cm as required, with the lowest ring having a bevelled edge. These tubes (eight per plot) were hammered into the ground at random, and then carefully lifted and separated into the 5-cm depth sections; corresponding sections from each plot were combined. Samples were taken on the day of application, on days 7, 14 and 28, and at longer intervals thereafter over 2.5 years. Depth of sampling was 10 cm initially, and then 15 cm after 336 days and 20 cm after 720 days when test cores indicated trace movement of flutriafol to these depths.

The samples were sieved to 6 mm, thoroughly mixed and the moisture content determined at 110 °C (2×20 g samples). Soils were stored if necessary at −10 °C prior to analysis.

2.5 Measurement of fungicides in the soil samples and on the paper discs

Extraction and analysis by high-pressure liquid chromatography (HPLC) were essentially by the procedure used for the laboratory incubations.[1] Differences were that soil samples (50 g, in duplicate) were extracted with methanol (200 ml), and then aliquots of the supernatant solution (50 ml) were evaporated and taken as previously through the Sep-Pak clean-up prior to HPLC. All results are corrected for the recovery factors,[1] and concentrations are expressed on a dry soil basis.

To estimate spray deposition on the filter-paper collecting discs, each disc was extracted in its 500-ml glass collection jar by orbital shaking with methanol (200 ml) for 4 h. Aliquots of extract (25 ml) were rotary evaporated to dryness and dissolved in the mobile phase (1.0 ml) for analysis by HPLC.[1] Recoveries by this procedure of compounds (250 µg, equivalent to the field rate) added to blank discs were essentially quantitative, and so no corrections were required.

2.6 Measurement of sorption to soil

Aliquots (10 ml) of fungicide solutions (5 µg ml^{-1} epoxiconazole and 10 µg ml^{-1} the others, in 0.01 M aqueous calcium chloride) were shaken in 30-ml glass centrifuge tubes with air-dried soils (2.0 to 4.0 g) sieved to 4 mm. After 2 h shaking, the suspensions were centrifuged and the amount of compound remaining in the supernatant solution was estimated by HPLC. The amount taken up by the soil was estimated by difference, and a K_d value calculated assuming a simple linear isotherm.

2.7 Simulation of fungicide persistence in soil

The concentrations of fungicides in field soils were simulated mainly using a version of the computer

Table 1. Soil sorption of the triazole fungicides and parameters used to simulate rates of degradation as a function of soil temperature and water content

		Rothamsted clay loam				Woburn sandy loam			
Fungicide	*Log K_{ow}*[a]	*K_d (ml g^{-1})*	*A (day)*	*B*	*E (cal mol^{-1})*	*K_d (ml g^{-1})*	*A (day)*	*B*	*E (cal mol^{-1})*
Flutriafol	2.3	1.04	1320[b]	0.01	5629[c]	1.53	274789	2.15	5629
Epoxiconazole	3.44	10.9	5370	0.5	2181	13.1	8530	0.85	3912
Propiconazole	3.72	5.87	53700	2.0	6687	6.9	2450	1.00	8427
Triadimefon	3.11	2.49	175	0.83	9045	3.38	189	0.77	7777
Triadimenol	3.2	1.72	5460	0.67	9087	2.09	182000	1.85	9422

[a] K_{ow} is the 1-octanol/water partition coefficient.
[b] This value appears low because the sensitivity to soil water has been arbitrarily set very low.
[c] Measured value unreliable for the Rothamsted soil, and so the Woburn value was used.

model CALF,[8] similar to that described by Walker.[9] The input data used in the simulations are given in Table 1 and the rates of application were those for the incorporated plots measured after deposition onto filter papers. Values of field capacity were obtained from measurements of soil water content made after a wet period in winter and the water content at -200 kPa pressure was taken as 60% of the value at field capacity. Field capacities were 20 and 13.8% for Rothamsted and Woburn, respectively. Initial soil water contents (10 and 4% for Rothamsted and Woburn, respectively) and sorption coefficients (Table 1) were measured values.

Coefficients (Table 1), including activation energies (E, in cal mol^{-1} for the model) used to calculate rates of degradation, were derived from complementary laboratory incubation experiments.[1] Rates of degradation were calculated as a function of soil water content (eqn (1)), in which H is half life and M is the soil water content.

$$H = AM^{-B} \tag{1}$$

The A and B parameters, representing respectively the notional half-life at a soil moisture of 1% and the sensitivity of degradation rate to soil moisture content, were calculated from half-lives measured at soil water contents corresponding to 60 and 80% of field capacity. The rate of degradation of flutriafol in the Rothamsted soil in the laboratory was insensitive to soil water content and so the corresponding B parameter was set to an arbitrary low value of -0.01. Daily rainfall and maximum and minimum air temperatures were measured at weather stations situated close (<1 km) to the field plots. Evaporation of water from soil and soil temperatures were calculated by the model from air temperatures. Some modelling was also done for the fallow plots receiving the surface sprays without subsequent incorporation, and these simulations were made with the model LEACH described by Walker[9] and utilising the same parameters as CALF.

3 RESULTS AND DISCUSSION

3.1 Field measurements of triazole fungicides

The application rates of the fungicides, as assessed by measurement from the paper-disc collection of the sprays (Fig 1) from the non-cropped plots, were on average 8% higher at Rothamsted and 19% lower at

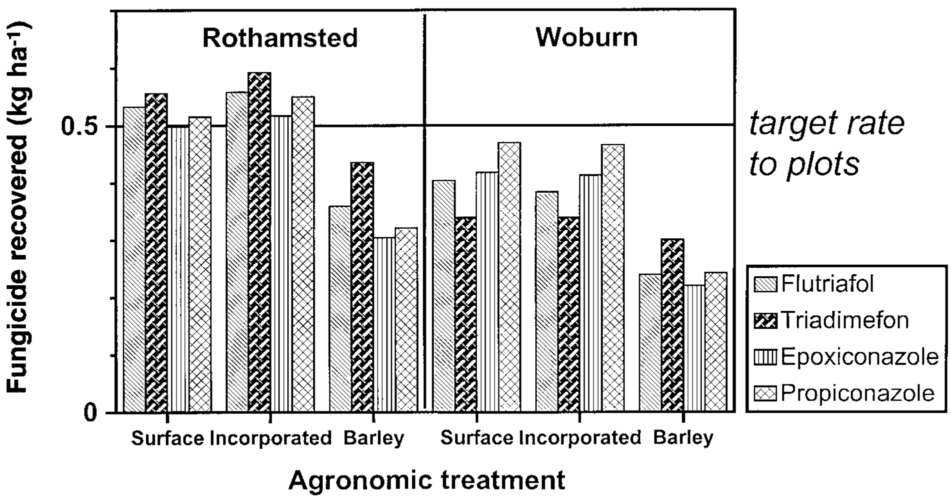

Figure 1. Fungicide recovered from paper discs on soil immediately following application of 0.5 kg AI ha^{-1} each.

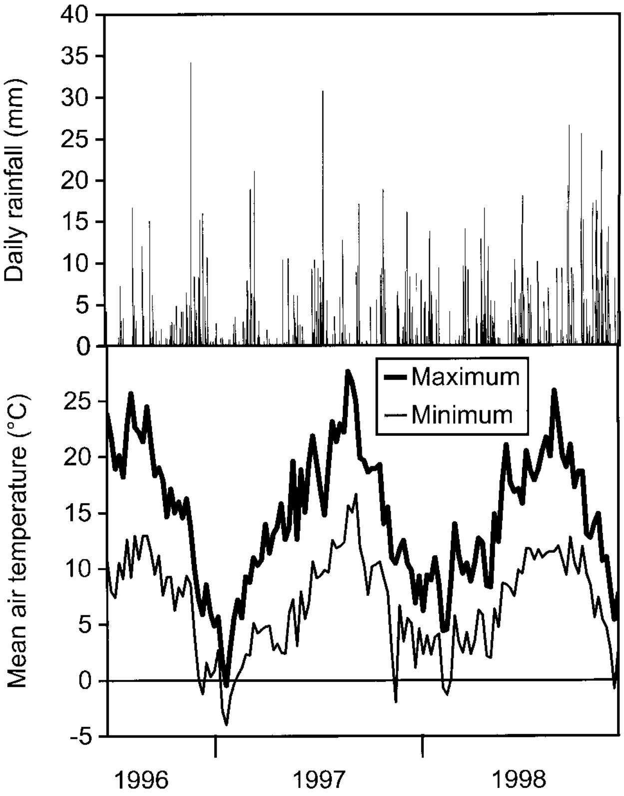

Figure 2. Daily rainfall and mean weekly maximum and minimum air temperatures at Rothamsted over the 2.5 years of the experiment.

Woburn than the intended 0.5 kg AI ha^{-1} each. The growing barley intercepted about 30% of the spray at Rothamsted, and slightly more at Woburn (38%) where the crop was more advanced. Incorporation put about one-third of the chemicals down to 5–10 cm at Rothamsted though somewhat less at Woburn, due to differences in the soil type and in the operation of the Roterra.

The weather over the subsequent 2.5 years of the experiment was similar at the two sites (40 km apart) and for Rothamsted is shown in Fig 2. The summers of both 1996 and 1997 were slightly warmer and drier than the average, though the overall rainfall was close to the long-term means of 69.5 and 63 cm per annum at Rothamsted and Woburn, respectively.

In the two field trials, triadimefon was rapidly converted by reduction to triadimenol, though traces of the former could be detected into the second year, indicating a possible redox equilibrium, as noted in the laboratory studies.[1] The other triazole fungicides were quite persistent and some could still be detected after 2.5 years (Fig 3). Flutriafol, epoxiconazole and triadimenol were the most persistent, with DT_{50} values of over 400 days irrespective of the agronomic treatment. Propiconazole was broken down more rapidly, though its DT_{50} values were still around 200 days at both sites. Flutriafol, the most polar and least sorbed of the five fungicides (Table 1), was somewhat leached, with comparable concentrations in the 0–5 and 5–10 cm layers after one year and with further leaching to 10–15 cm after two years, with traces then found at 15–20 cm (Fig 4). The other fungicides were little leached, with only traces ever found below 10 cm depth (results not presented) and most always found in the top 5 cm soil. Accordingly, the concentrations in soil (Fig 3) are averaged to 20 cm depth for flutriafol but to only 10 cm for the other compounds.

In general the field measurements were self-consistent and showed clear trends of loss, with good agreement between the replicate plots. Variable results were observed only occasionally, primarily for some of the propiconazole treatments at Woburn (Fig 3b); all apparently anomalous soil samples were re-analysed, but usually with no change in result, indicating that the variability lay in the application or in the sampling.

The effects of the different agronomic treatments were slight. Though the growing barley intercepted 30–38% of the spray, subsequent rain appeared to wash off some of these foliar deposits onto the soil. The highest concentrations in soil over the first few months were generally found for the plots receiving surface cultivation after fungicide application, though this was not observed for triadimefon. Indeed triadimefon immediately after application persisted at the highest concentrations in those plots receiving the spray onto the soil surface; it is assumed that the dryness of the surface soil limited the reduction process, which was more favoured by the shallow incorporation at which depth the soil would be moister.

Persistence of the other compounds was favoured by the incorporation brought about by cultivation, though this effect was barely noticeable for flutriafol. It is thought that this indicates that other loss processes are occurring initially for pesticides applied to the soil surface, which could include vapour loss or photolysis. This effect may be least for flutriafol because it is the most polar and hence most readily leached compound (Table 1), and so the early rains after application would cause sufficient leaching to give protection against such surface loss processes.

However, by two years after application, differences in amounts remaining between the surface-applied and shallowly incorporated treatments were very small for all compounds; it is thought that whilst incorporation protects against other loss processes at the soil surface, the moister soil at depth encourages subsequent breakdown, especially perhaps in a dry summer as occurred in 1996. At both sites, the behaviour of epoxiconazole seemed the most sensitive to the agronomic treatment.

Differences in behaviour of the compounds between the two sites were generally small. The more advanced spring barley at Woburn intercepted more of the spray, as discussed above, and the lower concentrations of compounds in the soil in the cropped plots continued into the second year, noticeable especially for epoxiconazole and propiconazole. Concentrations of triadimefon and then triadimenol in soil at Woburn were substantially less than at Rothamsted in the first year,

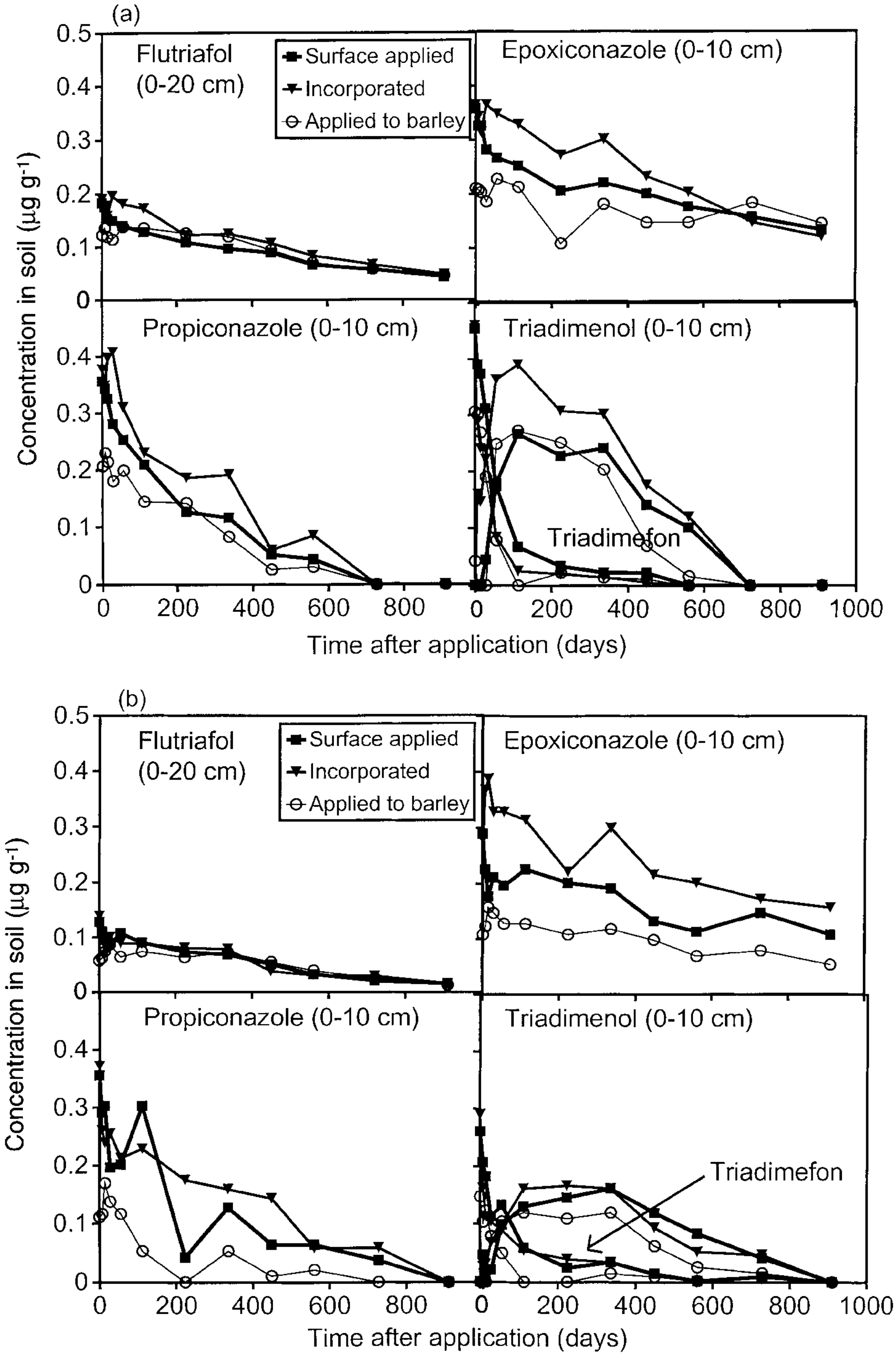

Figure 3. Persistence in topsoil of five triazole fungicides applied June 1996 in two field trials (a) Rothamsted clay loam (b) Woburn sandy loam.

and this is attributed to the fallow plots at the latter receiving *c*50% more triadimefon initially than did the Woburn plots as assessed by the paper collecting discs.

3.2 Modelling of the field behaviour

Fungicide persistence in the field was modelled mainly for the fallow plots receiving the surface spray followed by shallow incorporation (Fig 5). This application technique most closely resembles the laboratory incubation technique, and should allow the identification of surface-loss processes not included in the CALF programme. The rate constants used were generally independent of whether the fungicides were incubated singly or in admixture in soil.[1] Flutriafol was an exception in that it was degraded twice as quickly in the single-compound incubation and, though the field applications were of all fungicides, these lower half-lives were used in the simulations as flutriafol in the field was the most leached, thus becoming within a few months substantially separated from the other more sorbed fungicides. Some modelling was also done with LEACH for the plots receiving the surface spray but without soil incorporation; persistence here was slightly greater than for the incorporated plots due to the soil surface being drier than at depth (results not presented).

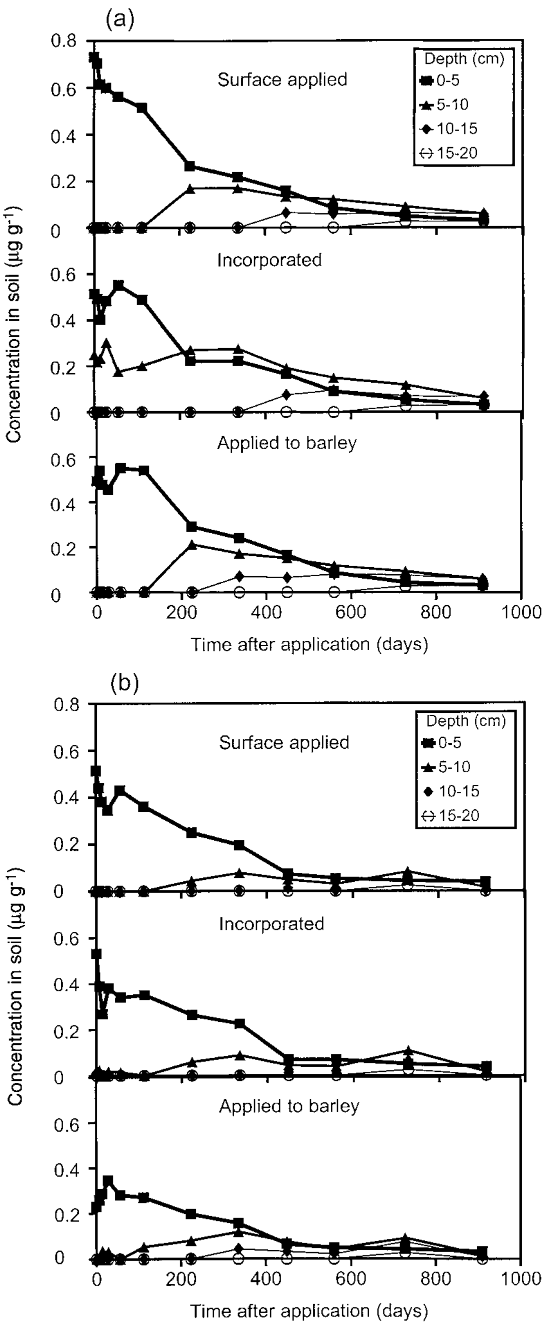

Figure 4. Persistence and leaching of flutriafol applied June 1996 in two field trials (a) Rothamsted clay loam (b) Woburn sandy loam.

The simulations generally over-estimated persistence of the fungicides, this effect being most marked for the more persistent compounds, with behaviour of the relatively less persistent propiconazole being well modelled. Concentrations found in field soils following surface spray application were much less than predicted, this difference mirroring those noted above with the additional feature of a noticeable drop in concentration over the first few days after spraying. This confirms that another process not included in the modelling, such as photolysis and/or volatilisation, must be occurring on the soil surface. The first rainfall may have caused sufficient leaching to stop or greatly slow this soil-surface phenomenon. No new peaks appeared in the HPLC chromatograms that could be attributed to breakdown products as might occur following photolyis. Jenkyn *et al*[10] noted that, in field trials with triadimenol, control plots of cereals adjacent to sprayed plots showed reduced fungal infection, which was attributed to movement by volatilisation. Triadimefon showed similar effects in glasshouse trials.[11] Thus, despite their quite low vapour pressure, it is possible that volatilisation may contribute appreciably to this initial loss in many situations.

Triadimenol showed the most striking deviations from the predictions, with none being found in the field at Rothamsted after 24 months despite long half-lives measured in the laboratory incubations even at 18 °C in moist soils. Likewise, in the field in the first year it was also persistent, but at Rothamsted it could not be detected by the end of the second year. The analytical method easily had adequate sensitivity to detect the field concentrations predicted using the laboratory measurements, and so this more rapid loss in the second year is a genuine effect. This observation is consistent with the earlier report by Bromilow *et al*[5] that triadimenol could not be detected in the field 22 months after the last of 12 annual applications of triadimefon at $0.25\,kg\,ha^{-1}$ even though the laboratory half-life at 15 °C of triadimenol in this soil was about one year. The reason for this is not known. Epoxiconazole and flutriafol were found in the field even 30 months after the single $0.5\,kg\,ha^{-1}$ application, but at concentrations less than those simulated.

Jurado-Exposito and Walker[12] measured the degradation of four herbicides in two sandy loam soils, under conditions of either constant temperature and soil moisture or with cycling of these parameters. Under constant conditions or with temperature cycling between 10° and 20 °C, breakdown of all four herbicides followed first-order kinetics; with cycling of the soil moisture, breakdown of three compounds followed the expected behaviour, but the breakdown of propyzamide was initially somewhat slower than expected but after 35 to 40 days accelerated to give very rapid losses. This was ascribed to the development of microbial populations able to degrade propyzamide, this adaptation process being in some way favoured by the variable soil-moisture regime. No such rapid losses were observed in our triazole studies, though temperature cycling could have encouraged the faster breakdown observed in the field.

4 CONCLUSIONS

Several of the triazole fungicides examined were persistent both in the field and in soil incubations in the laboratory. However, these compounds were generally somewhat less persistent at both field sites studied than expected from the incubations. Simulation helped quantify these differences and allowed a distinction to be made between two contributing factors. The first of these was an initial loss of up to

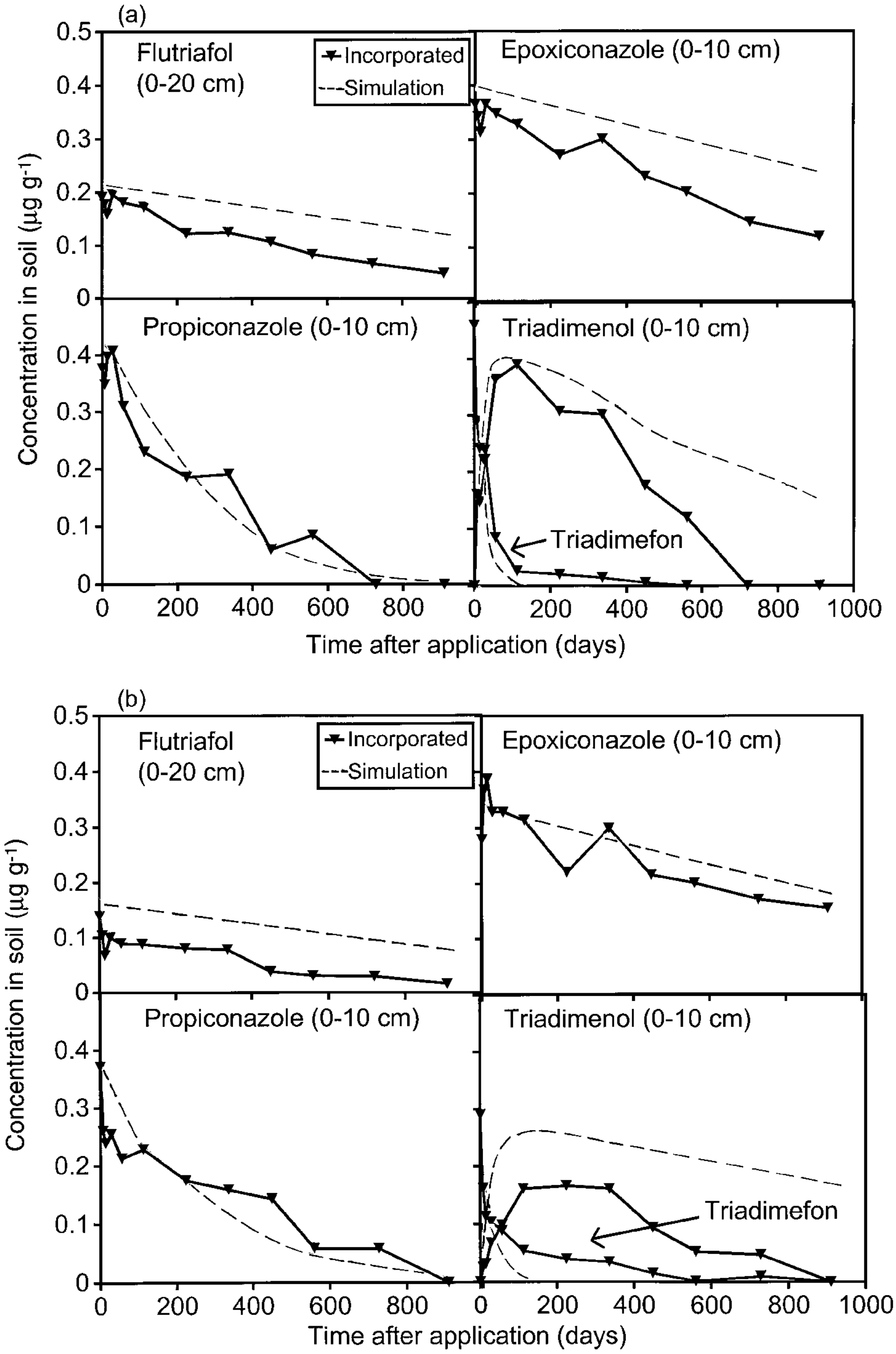

Figure 5. Simulation of the persistence in topsoil of five triazole fungicides applied June 1996 in two field trials and shallowly incorporated by cultivation (a) Rothamsted clay loam (b) Woburn sandy loam.

about 50% by 28 days after spraying, which was eliminated by soil incorporation and so attributed to a surface-loss process such as photolysis and/or volatilisation. The second process was long-term, particularly marked for triadimenol, whereby loss in the field was somewhat more rapid than in the laboratory. Though the explanation for this is unclear, it is not thought to be an artifact caused by the soils losing their activity in the laboratory tests, for first-order kinetics were observed over the 720 days of incubation. If anything, the rate of loss in the field appeared to increase on moving into the second year, and it might thus be that a critical lower concentration was reached below which degradation was somewhat faster and/or that field conditions favoured the development of a microbial population able to degrade these compounds.

Though these triazole fungicides are indeed persistent in the field in comparison to most modern pesticides, these additional loss processes will aid in mitigating accumulation of residues in soil following repeated applications at modest rates. Furthermore, measurements of persistence in soil in laboratory tests, themselves difficult for persistent compounds, may not give an accurate basis on which to predict losses in the field. Thus detailed field studies should always be available to complement and confirm measurements in laboratory incubations and predictions therefrom.

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